

DETERMINATION OF MECHANISM OF THERMAL DECOMPOSITION OF Mg, Ca AND Zn HYDRAZIDOCARBONATES BY EVOLVED GAS ANALYSIS

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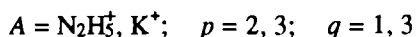
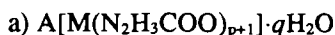
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Hydrazo-carbonates are complex compounds and products of the reactions between solutions of metal ion and solutions of hydrazido-carbonic acid. The decomposition of $\text{Mg}(\text{N}_2\text{H}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$, $\text{Ca}(\text{N}_2\text{H}_3\text{COO})_2 \cdot \text{H}_2\text{O}$ and $\text{Zn}(\text{N}_2\text{H}_3\text{COO})_2$ in inert atmosphere were studied. By classical thermoanalytical methods and data on the composition of the intermediates and final products the mechanisms of the thermal decomposition could not be resolved therefore also evolved gas analysis was used (EGA). The first step of thermal decomposition of Ca and Mg hydrazidocarbonates is dehydration. With the heating the decomposition of the hydrazido-carbonates proceeds under evolution of the ammonia, carbon monoxide and/or nitrogen and carbon dioxide giving as the intermediates for calcium and magnesium compounds the corresponding carbonates oxides as the final products. The zinc compound decomposes to the oxide, ZnO but also zinc cyanamide was detected during to the thermal treatment.

Keywords: complexes, EGA, mechanism of thermal decomposition

Introduction

Hydrazidocarbonates are complex compounds products of the reactions of aqueous solutions of metal cations and solutions of hydrazidocarbonic acid or hydrazinium (1+) hydrazidocarbonate [1, 2]. Besides the metal cation and hydrazidocarbonato group the constituents of the complexes are also hydrazine, hydrazinium (1+) ions and water. Few compounds are also known where hydrazinium (1+) ions are replaced by potassium ions. All these constituents lead to a great variety of different types of hydrazidocarbonates:





$$p = 1, 2, 3; \quad q = 0, 0.5, 1, 2, 3; \quad r = 0, 1, 2$$

Metals wide range of metal cations that form hydrazidocarbonates:

a) Sc, Fe, Co, Ni and Zn

b) Li, Na, Tl, Mg, Ca, Ba, Cr, Mn, Fe, Co, Ni, Cu, Zn, Cd, Y, La, lanthanides except Pm and U.

Thermal properties of these complexes differ regarding the central cation, the composition, type of hydrazidocarbonate and the atmosphere that was used during the experiments. The inclusion of a strong reductant into the complex, e.g. N_2H_3^- and besides that in some cases also additionally N_2H_4 or N_2H_3^+ leads during thermal analysis in air to very exothermic reactions, giving as the end products generally the corresponding metal oxides. The TG curves of the hydrazidocarbonates exhibit in an inert atmosphere more complex behaviour and a greater variety of intermediates and end products as well. Besides the metal oxides also pure metal powders can be obtained and in some cases mixtures or products that have not been completely characterised yet. The decomposition processes are in an inert atmosphere influenced primarily by the central cation and the type of hydrazidocarbonate. These factors focused our studies on thermal behaviour of hydrazidocarbonates mainly on decompositions in an inert atmosphere.

The complexity of the thermal decomposition of hydrazidocarbonates directed us to select for a study the simplest type of these compounds where no additional complexity is introduced by N_2H_4 or N_2H_3^+ constituents. For these studies a group consisting of $\text{Mg}(\text{N}_2\text{H}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$, $\text{Ca}(\text{N}_2\text{H}_3\text{COO})_2 \cdot \text{H}_2\text{O}$ and $\text{Zn}(\text{N}_2\text{H}_3\text{COO})_2$ was taken. Besides chemical analysis of the intermediates and end products also X-ray powder diffraction, IR and evolved gas analysis were used.

Experimental

Magnesium hydrazidocarbonate dihydrate and calcium hydrazidocarbonate monohydrate were prepared on the basis of literature data [3, 4] from 15% aqueous solution of hydrazine previously saturated with carbon dioxide and a solution of a metal chloride. For the synthesis of zinc hydrazidocarbonate a new procedure was used consisting of a reaction carried out at elevated temperatures ($80^\circ\text{--}90^\circ\text{C}$). This shortens the time of crystallization from 4 to 5 days as needed for the previously reported synthesis [3, 5] to almost instantaneous reaction.

The amount of the metals in the starting compounds, intermediates and the end products was determined by volumetric titration by EDTA [6]. Hydrazine was determined by potentiometric titration by potassium iodate [7] and the carbonate content was determined gravimetrically.

Thermal properties of the samples were determined by the Netzsch STA 409 apparatus at the following conditions: starting temperature 20°C, heating rate 4 deg·min⁻¹, sample weight 100 mg (TG/DTA) and 1000 mg (EGA), atmosphere dry and oxygen free argon (Oxisorb), flow rate 6 l/h.

Evolved gas analyses were performed by set up consisting of the thermobalance STA 409 connected to Inficon Quadrex 200SCU Leybold Heraeus mass spectrometer. The carrier gas from the furnace of the thermobalance was led to MS through a 5 m long stainless steel capillary with the internal diameter of 0.6 mm. Capillary was heated to 120°–130°C to prevent condensation. The inlet pressure at MS was 10 mbar, and the operating pressure in the MS 1.10⁻⁴ bar. Scanning time for the selected mass range from 1 to 50 AMU was 7.59 seconds, gain 6·10⁻¹¹ A. Bar spectra were every 30 seconds transferred to and saved on a personal computer and these data were after the analysis converted to a graphical form. X-ray diffraction analyses were carried out on Philips PW-1710 diffractometer (30 mA, 40 kV and CuK_α-radiation). CD-ROM data base PDF2 set 1–39 was used for the identification of the intermediates and final products. Solid film technique and an 1720X Perkin-Elmer apparatus were used for obtaining IR spectra in the range from 4000 to 220 cm⁻¹.

Results

The results of the thermal analysis in pure argon atmosphere are presented in Table 1, Figs 1 and 2. The comparison of the thermal stability of all three starting compounds is not sensible since the two of them are hydrates. During heating both two hydrates lose water and anhydrous hydrazidocarbonates are obtained. Mg(N₂H₃COO)₂·2H₂O dehydrates in the temperature range from 127.6° to 189.7°C with the calculated 17.12% and obtained mass loss of 18.3% (Table 2). X-ray powder diffraction data revealed that the anhydrous magnesium hydrazidocarbonate is not isostructural with the hydrated form. This is in accordance with the known structural data for manganese hydrazidocarbonate dihydrate [8], Mn(N₂H₃COO)₂·2H₂O that is isostructural with Mg(N₂H₃COO)₂·2H₂O. This structure consists of chains formed by two types of trans, cis, cis-octahedral chelates, bound together in the chain by bridging hydrazidocarbonato groups. Since part of the water molecules is co-ordinated to the metal, their

removal from coordination sphere during dehydration also alters the structure of the hydrazidocarbonate. The other part of water is water of crystallization.

Table 1 Result of TG/DTA analysis

Mg	$\Delta m / \%$	$T_i / ^\circ\text{C}$	DTG $^\circ\text{C}$	DTA $^\circ\text{C}$
1.step	18.3	127.6	144.8	147.6(-)
2.step	42.0	256.7	331.8	329.6(-)
3.step	16.4	400	532.3	530.2(+) and 638.9(-)
Total	76.7			
Ca				
1.step	8.4	89.7	112.8	115.4(-)
2.step	38.5	220.0	305.0	306.6(+)
3.step	3.5	428.0	474.0	488.1(+)
4.step	17.9	560.0	778.6	785.5(-)
5.step	3.9	1068.0	1167.0	1073.9(+) and 1175.0(-)
Total	72.2			
Zn				
1.step	54.0	186.2	340.1	239.5(-) and 324.8(-)
2.step	5.6	482.8	607.8	620.6(-)
3.step	27.4	748.3	922.1	920.0(-)
Total	87.0			

+ exothermic reaction, - endothermic reaction

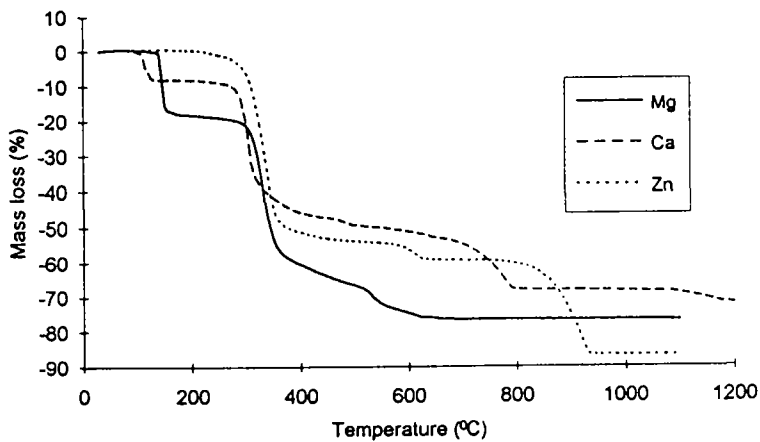


Fig. 1 TG analysis of hydrazidocarbonates

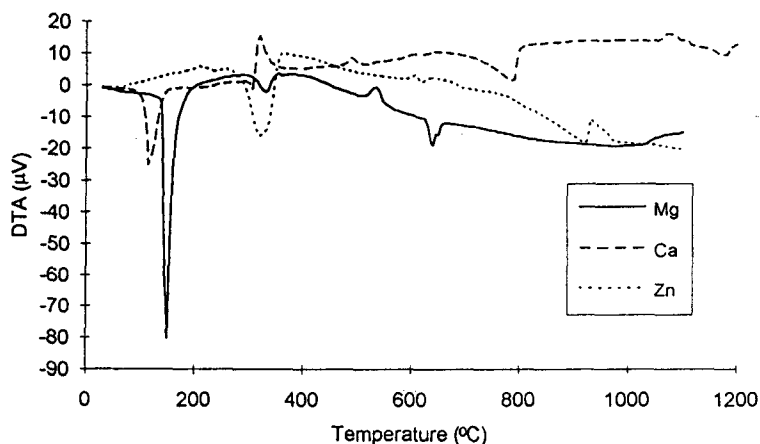


Fig. 2 DTA analysis of hydrazidocarbonates

Similarly the sample of $\text{Ca}(\text{N}_2\text{H}_3\text{COO})_2 \cdot \text{H}_2\text{O}$ loses water in the range from 89.7° to 112.8°C with the calculated and obtained mass losses of 8.65 and 8.4% respectively. The dehydration was in both cases confirmed also by chemical analysis of the intermediates.

Table 2 Chemical analysis of starting compounds, intermediates and end products

	<i>M</i> / %		N_2H_4 / %		CO_2 / %	
	Found	Calc.	Found	Calc.	found	calc.
$\text{Mg}(\text{N}_2\text{H}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$	11.7	11.55	30.3	30.48	41.9	41.84
1. intermed. 220°C	14.2	13.94	36.8	36.78	50.1	50.49
2. intermed. 410°C	26.9	(28.83) MgCO_3			27.5	52.19
2. intermed. 517°C	38.8				11.2	
End prod. 800°C	50.5	(60.30) MgO				
$\text{Ca}(\text{N}_2\text{H}_3\text{COO})_2 \cdot \text{H}_2\text{O}$	19.8	19.25	30.5	30.78	42.4	42.29
1. intermed. 220°C	21.7	21.09	32.8	33.72	48.0	46.30
2. intermed. 490°C	39.6	(40.05) CaCO_3			31.4	43.96
3. intermed. 680°C	43.2				31.7	
End prod. 1200°C	64.2	(71.47) CaO				
$\text{Zn}(\text{N}_2\text{H}_3\text{COO})_2$	30.3	30.34	29.1	29.75	40.1	40.86
1. intermed. 420°C	64.5	(62.04) ZnCN_2			4.0	
2. intermed. 730°C	74.4				0.9	
End prod. 1000°C	81.0	(80.34) ZnO				

Comparison of the initial temperature of $\text{Zn}(\text{N}_2\text{H}_3\text{COO})_2$ with the further decomposition of both dehydrated compounds reveals that magnesium hydrazidocarbonate is the most stable ($T_i = 256^\circ\text{C}$) being followed by calcium (220°C) and zinc (186°C) compounds. Subsequent decomposition processes that occur at higher temperatures differ for all three samples appreciably.

For the magnesium compound two more intermediates could be isolated during the thermal decomposition. The second intermediate obtained at 410.0°C was of a pale green colour. Chemical analysis revealed that hydrazine is not present any more and that the sample besides the magnesium content of 26.9% contains also 27.5% of carbon dioxide. The difference to 100%, e.g. 45.6% has not been fully characterized yet. The diffraction data reveal amorphous nature of the intermediate with only the strongest peak for MgO raised above the background. As shown in Fig. 3 EGA displays the evolution of gases with the AMU of 17, 28 and 44 corresponding to ammonia, nitrogen or carbon monoxide and carbon dioxide respectively. Neither hydrazine nor hydrogen were detected in the evolved gases. Low sensitivity of the MS for hydrogen could be the course for omission of hydrogen detection. The third intermediate was isolated at 517.0°C and is pale yellow in colour. The content of carbon dioxide diminishes to 11.2% that is in accordance with the EGA data. The X-ray data show increased peak for magnesium oxide and some unidentified peaks. The end product of the thermal decomposition is magnesium oxide mixed with another residue giving peaks on the diffractometer that so far could not be assigned to any known compound.

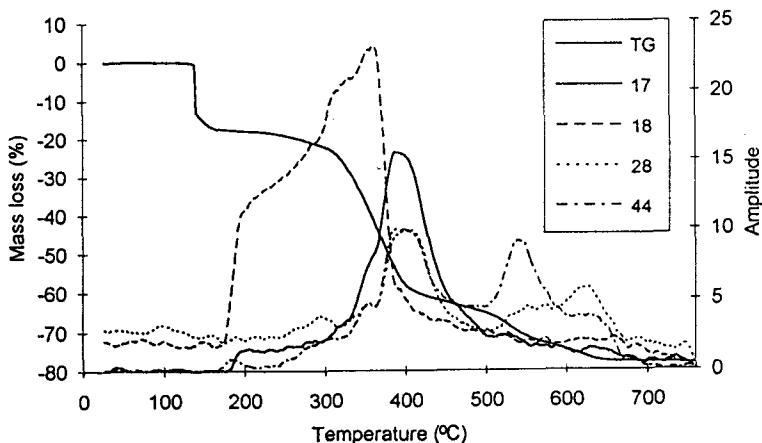


Fig. 3 EGA of $\text{Mg}(\text{N}_2\text{H}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$

After the dehydration the anhydrous calcium hydrazidocarbonate further decomposes in several steps (Fig. 4) in the product isolated at 490°C that formed after the evolution of ammonia, nitrogen or carbon monoxide and in lesser extent

carbon dioxide by chemical analysis only calcium and carbon dioxide were detected. Diffraction data show that the major part consists of calcium carbonate in the calcite form. The product obtained at 680°C contains practically the same percentage of carbon dioxide, e.g. 31.7% as the preceding intermediate but higher content of the metal that is the consequence of evolution of a gas with AMU 28. The crystallinity also increased giving more peaks that could not be assigned. The end product is predominantly calcium oxide but on a diffractogram also some other unidentified peaks occur.

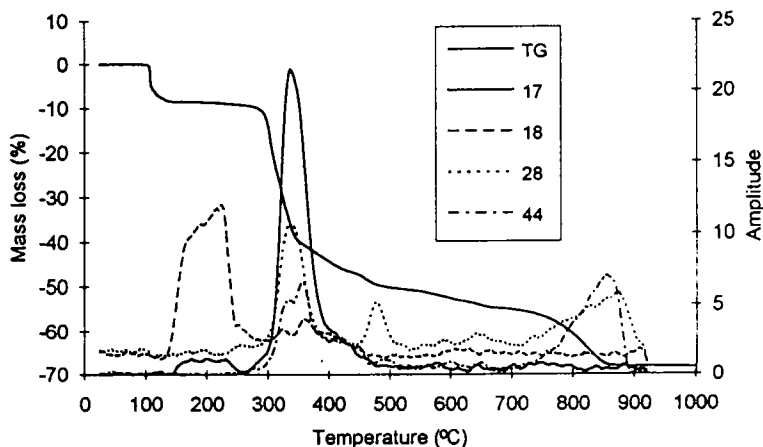


Fig. 4 EGA of $\text{Ca}(\text{N}_2\text{H}_3\text{COO})_2 \cdot \text{H}_2\text{O}$

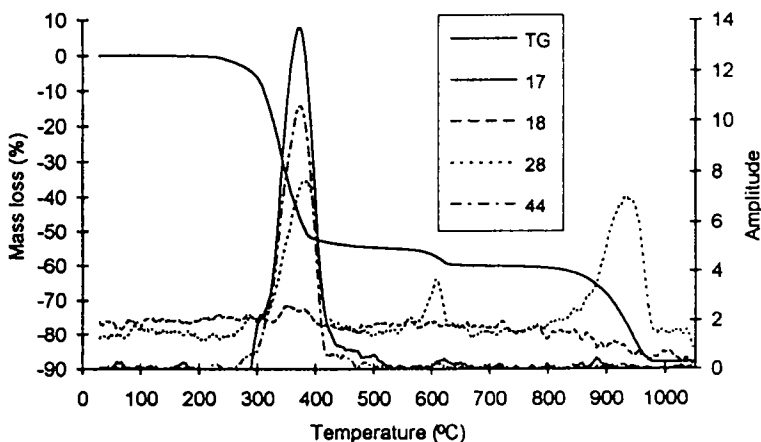


Fig. 5 EGA of $\text{Zn}(\text{N}_2\text{H}_3\text{COO})_2$

Zinc hydrazidocarbonate decomposes in three steps (Fig. 5). During the first one the evolution of ammonia, nitrogen or carbon monoxide and carbon dioxide is observed. Only 4% of carbon dioxide were determined in the residue. X-ray of the first intermediate reveals the presence of zinc oxide and cyanamide, $ZnCN_2$. Next step is attained after the evolution of a gas with AMU 28. The diffraction data show as in the previous case presence of zinc oxide and an enhancement of the cyanamide content. The last step is completed after the evolution of a gas with AMU 28. The residue obtained at $1100^\circ C$ is mainly zinc oxide. The cumulative mass loss of 87.0% signals that also some zinc has left the crucible since the calculated mass loss for formation of zinc oxide should be 62.21%. During the thermal decomposition probably some zinc metal or its volatile compound formed which evaporated at these temperatures. The melting point of zinc is $419.6^\circ C$.

Conclusion

Although the hydrazidocarbonates of magnesium, calcium and zinc are apparently the least complex of the hydrazidocarbonates, their decomposition reactions in an inert argon atmosphere do not follow this assumption. In the case of both two hydrates anhydrous compounds can be prepared by the thermal treatment of the starting compounds. The next step of the decomposition is accompanied by the evolution of ammonia and nitrogen due to the decomposition of hydrazido group. Nitrogen, carbon monoxide or both gases and carbon dioxide evolve during heating to the final temperatures. Interesting transformation of hydrazidocarbonato group to carbonate could be observed in the case of calcium compound. This is also probable for the magnesium compound although the magnesium carbonate was probably amorphous and evaded the detection by X-ray diffraction. Zinc cyanamide was observed in the decomposition sequence of the zinc compound. The end products are impure magnesium, calcium and zinc oxide.

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Zusammenfassung — Hydrazocarbonate sind Komplexverbindungen und Reaktionsprodukte der Reaktion zwischen Lösungen von Metallionen und Lösungen von Hydrazidocarbonsäure. Es wird die Zersetzung von $\text{Mg}(\text{N}_2\text{H}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$, $\text{Ca}(\text{N}_2\text{H}_3\text{COO}) \cdot 2\text{H}_2\text{O}$ und $\text{Zn}(\text{N}_2\text{H}_3\text{COO})_2$ in inerter Atmosphäre untersucht. Anhand klassischer thermoanalytischer Methoden und Daten über die Zusammensetzung von Zwischen- und Endprodukten konnte kein Mechanismus für die thermische Zersetzung gefunden werden, weshalb auch eine Analyse der freigesetzten Gase (EGA) durchgeführt wurde. Der erste Schritt der thermischen Zersetzung von Ca- und Mg-Hydrazidocarbonaten ist die Dehydratation. Bei Erhitzen erfolgt die Zersetzung von Hydrazidocarbonaten unter Freisetzung von Ammoniak, Kohlenmonoxid und/oder Stickstoff und Kohlendioxid als Zwischenprodukt für Calcium- und Magnesiumverbindungen, wobei die entsprechenden Carbonatoxide als Endprodukte entstehen. Die Zinkverbindung zerfällt in das Oxid ZnO , aber auch Zinkcyanamid kann beim Erhitzen beobachtet werden.